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Disclaimer

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Supporting Information Placeholder

ABSTRACT: Second-generation cobalt and zinc coordination architectures were obtained from efforts to stabilize extremely sensitive and energetic transition metal hydrazine perchlorate ionic polymers. Partial ligand substitution with the tridentate hydrazinecarboxylate anion afforded polymeric 2D flat-sheet structures never before observed for energetic materials. Carefully balanced reaction conditions allowed the retention of the non-coordinating perchlorate anion in the presence of a strongly chelating hydrazinecarboxylate ligand. High-quality X-ray single crystal structure determination revealed that the metal coordination preferences lead to different structural motifs and energetic properties, despite the nearly isoformulaic nature of the two compounds. Energetic tests indicate highly decreased sensitivity while DFT calculations suggest high power output of these remarkable structures.

Recently we reported new ionic polymeric energetic architectures with tremendous power output.[1] These Ni and Co hydrazine perchlorate (NHP and CHP) energetic materials (EMs) provide the power of conventional secondary explosives while avoiding the use of heavy metals still common in primary energetics. Unfortunately, the high sensitivity of NHP and CHP may preclude their commercial use. Beyond their energetic properties, the NHP and CHP crystal structures demonstrated the overlooked potential of hydrazine as a ligand for solid state architectures. They were the first crystal structures with hydrazine as the sole inner-sphere ligand and form one-dimensional chains with just one bridging hydrazine molecule defining the backbone of the coordination polymer (**Figure 1a**). The low rigidity characteristic of such linear polymeric structures combined with fairly weak Ni- or Co-nitrogen bonds and high hydrazine:metal ratio yielded highly sensitive compounds, especially so in the case of NHP. Continuing our tandem efforts in exploring the structural potential of hydrazine as a ligand for coordination polymers and the preparation of improved energetic materials, we present here an account of two novel two-dimensional polymeric cobalt and zinc based high-nitrogen rich architectures, where ligand structural modification results in considerable reduction of sensitivity.

Examination of the NHP and CHP poly-metalhydrazine perchlorate[1] structures reveals several directions for possible structural modifications. The easiest modification, anion substitution, is not viable since the choice is restricted to oxidizing nitrate or perchlorate anions. Both Ni and Co hydrazine nitrates were previously prepared yielding only modest energetic properties,[2] which indicates that using nitrate instead of perchlorate will sacrifice oxidizing capacity too severely. Azides, which are commonly employed in EMs,[3] will not allow the most energy efficient utilization of the oxidizable hydrazine scaffold due to their non-oxidizing nature. Theoretically, the metal core of the coordination polymers can be substituted by other transition metals thus changing the electronic distribution in the complex, or alternatively the energetic ligand itself can be modified. The shortcoming of metal substitution lies in the fact that only a limited number of combinations are practical or even possible. A fairly small number of metals prefer nitrogen-based coordination, as opposed to oxophilic metals, which will readily hydrolyze to form more favorable M-O bonds. The choice is further narrowed by the desire to avoid the use of toxic heavy metals or expensive noble metals. Finally, the ligand modification can only be carried out in such a way as to allow the overall preservation of the polymeric backbone, which confers structural and chemical stability.

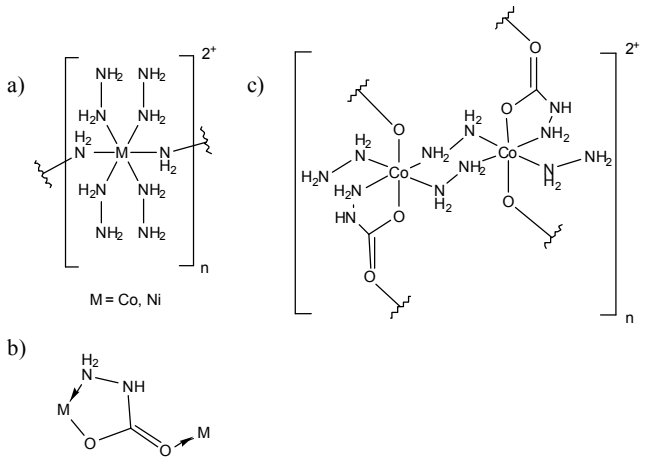

Figure 1. a) Schematic of NHP and CHP motif; b) binding mode of hydrazinecarboxylate; c) Schematic showing cobalt dimers

Hydrazine is almost ideal as a ligand for energetic coordination polymers owing to its bidentate nature, all gaseous decomposition products, and the absence of any oxidizable carbon, which would reduce the oxygen balance of the final EM. However, the previously prepared NHP and CHP proved highly sensitive and extremely powerful – a dangerous combination, hence the need for a ligand substitution that would somewhat

attenuate the energetic properties. Consequently, our requirement for hydrazine modification is to retain the polydentate nature of the ligand while avoiding alkyl or aryl substituents on the hydrazine moiety. The spontaneous and unanticipated reaction of hydrazine with atmospheric carbon dioxide furnished an excellent candidate: hydrazinecarboxylic acid.

Hydrazine is known to react with carbon dioxide yielding hydrazinecarboxylic acid.[4] The hydrazinecarboxylate anion can serve as a bidentate or tridentate ligand and consequently can be used for the construction of coordination polymers.[5] Due to its chelating nature, however, it often forms stable, monomeric *bis*[6] or *tris*[4,7]-hydrazinecarboxylate complexes with transition metals. Nevertheless, crystallographic studies demonstrate that the coordination chemistry of hydrazinecarboxylate is much richer than for unsubstituted hydrazine since it can coordinate to the metal center in at least three different ways.[4] The arrangement of interest to this investigation results from the carbonyl oxygen electron pair interaction with the neighboring metal center resulting in hydrazinecarboxylate linkage of two metal centers (**Figure 1b**). The carboxylate carbon serves as a latent source of carbon dioxide decreasing power density and desensitizing the compound. The combination of the oxidizing perchlorate anion, the highly energetic bidentate hydrazine ligand, and the stabilizing and bridging hydrazinecarboxylate chelate appears to fully satisfy the design requirements for practical, stabilized polymeric energetic compounds.

In retrospect, the foremost challenge in successfully synthesizing the above design elements arises from the need to preserve the non-coordinating perchlorate anion in the presence of the competitive, chelating hydrazinecarboxylate anion. This became clear following synthetic attempts which involved treating a metal perchlorate/hydrazine solution with CO_2-saturated hydrazine; this approach merely led to precipitation of metal hydrazinecarboxylate complexes. In fact, similar methods have been employed to obtain monomeric transition metal hydrazinecarboxylates.[7] Furthermore, examination of crystal structures reported in the Cambridge Structural Database including a metal bonded to a hydrazinecarboxylate reveals that no structures have been reported in which a metal-hydrazincarboxylate crystallizes alongside another ancillary anion. In order to incorporate the perchlorate ion in the structure, the concentration ratio of perchlorate:hydrazinecarboxylate must be greatly increased. Instead of saturating hydrazine solution with carbon dioxide, simple absorption of atmospheric carbon dioxide by metal hydrazine perchlorate solutions provides the correct balance. On the order of hours for cobalt and tens of hours for Zn, crystalline energetic products formed; single crystal X-ray diffraction identified these as Co- and Zn- hydrazine hydrazinecarboxylate perchlorate complexes ($Co(N_2H_3CO_2)(N_2H_4)_2ClO_4 \bullet \frac{1}{2}H_2O$, $Zn_2(N_2H_3CO_2)_2(N_2H_4)_3(ClO_4)_2 \bullet H_2O$, **CHHP** and **ZnHHP**, respectively). Crystallographic statistics are summarized in the SI.

CHHP crystallizes in the monoclinic P2(1)/c space group with two formula units per asymmetric unit and four formula units per unit cell. CHHP forms a sheet polymer in the solid state composed of distorted octahedral metal centers bearing mixed coordination spheres. The sheets lie parallel to the crystallographic *bc*-plane and stack along the crystallographic *a*-axis with layers of perchlorate anions between the sheets. Each metal bears three hydrazine ligands – one coordinates in a terminal monodentate mode while two others bridge to a second metal center to form cobalt-dimers (shown schematically in **Figure 1c**). Each metal also bears two hydrazinecarboxylate ligands – one chelates the cobalt through the terminal nitrogen and one oxygen; the other hydrazinecarboxylate coordinates to the metal center in a monodentate mode through an oxygen. Hence, every hydrazinecarboxylate is tri-dentate (**Figure 1b**) and bridges two metal centers parallel to the *c*-axis. The resulting sheet is a web composed of mixed-ligand cobalt dimers (**Figure 2a**). The perchlorate anion is disordered almost equally between two positions with both components contributing to hydrogen bond network holding the sheets together.

ZnHHP crystallizes in a triclinic P-1 space group with two formula units per asymmetric unit and four formula units per unit cell. Although ZnHHP has a similar formula to CHHP, it manifests a different and highly varied coordination chemistry of the zinc metal center. ZnHHP forms a 2D polymeric sheet, which comprises three different zinc coordination environments (**Figure 2b**). Portions of the 2D sheet polymer look like a "ladder" motif. The "rungs" are composed of octahedral zinc centers, each with two monodentate, terminal hydrazine units which are *trans* to each other and two bridging hydrazinecarboxylate ligands, also mutually *trans*. The "arms" of the ladder are made by two additional zinc centers – these form a network of shared hydrazine and hydrazinecarboxylate ligands. One zinc center has a distorted square pyramidal coordination sphere in which the "base" of the pyramid is defined by bonds to two hydrazine ligands and one bidentate hydrazinecarboxylate ligand while the apical bond of the pyramid joins this zinc center to the "rung" of the ladder structure. The final zinc center is octahedral with four equatorial hydrazine ligands and two axial bonds to hydrazinecarboxylate oxygens.

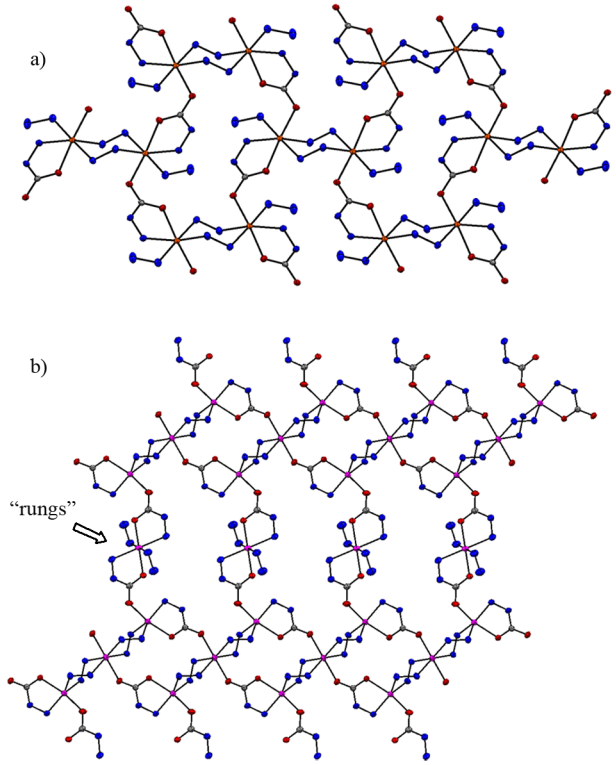

Figure 2. a) Partial packing diagram of CHHP showing sheet structure parallel to the *bc*-plane. b) Partial packing diagram of ZnHHP sheet showing ladder motif. Orange = Co, Pink = Zn, Blue = N, Red = O, Grey = C. In both graphics, perchlorate anions and co-crystallized water have been omitted for clarity.

As in the case of CHHP, every hydrazine carboxylate is tridentate and binds to two metal centers.The nickel analogue of these compounds was not obtained due to high sensitivity of

NHP, as even the solution can be explosive. The series cannot be extended to copper due to the fact that copper perchlorate vigorously reacts with hydrazine at room temperature.

The sensitivity of CHHP and ZnHHP assessed qualitatively by the means of a home-made drophammer apparatus and spark tests show marked decrease compared with previously studied NHP and CHP. CHHP can still be initiated by spark, while ZnHHP is insensitive to such stimulus. CHHP detonates on exposure to flame while ZnHHP deflagrates. The differential scanning calorimetry (DSC) plots show single exotherms corresponding to decomposition with no phase changes observed; the decomposition temperatures of CHHP and ZnHHP (231°C and 293°C, respectively) are much higher than observed for CHP (194°C). The observed higher stability of CHHP and ZnHHP relative to NHP and CHP prompted us to perform computational studies on these compounds to assess whether these complexes had retained sufficient power to serve effectively as energetic materials.

In order to estimate the heat of detonation (ΔH_{det}) of these two new explosives and see how they compare with the heats of commonly known energetic materials we adopted the methodology recently employed for NHP and CHP.[1] In this method we use Density Functional Theory (DFT) to compute the energy of detonation $\Delta E_{DFT,det}$ (the difference in total energy between a crystal unit cell of the energetic material and the sum of the total energy of the products), from which ΔH_{det} is estimated by using a linear correlation developed from known detonation heats of eleven commonly used high explosives.[1] As in ref. [1], the DFT calculations for CHHP and ZnHHP were performed using the code DMol^3 (ref. 20 from our JACS) under 3D periodic boundary conditions employing the Monkhorst-Pack multiple k-point sampling of the Brillouin-zone (ref. 22 from our JACS) and the Perdew-Becke-Ezerhoff (PBE) exchange-correlation function (ref. 21 from our JACS). Given large uncertainties in the positions of H atoms in the XRD determined structures, the H-atom positions were optimized by DFT, while the heavy atoms were kept constrained in their XRD-assigned positions. In order to represent the inherent disorder in position of the ClO_4 groups and water molecules in the CHHP unit cell, we considered all possible distinct combinations of positions and determined the average value of the detonation heat. However, the variation in detonation heats due to variation in the positions of ClO_4 and water was found to be small, less than 1.5%, and simply using one of the representative structures would have led to the same conclusions as obtained (below) from the averaged heat of CHHP.

For both CHHP and ZnHHP, water, nitrogen, carbon dioxide and ammonia were assumed to be the final products of decomposition of the organic part of the framework while the formation of mixture of a metal oxides and chlorides was assumed to be governed by the stoichiometric shortfall of oxygen. The complete decomposition reactions considered for CHHP and ZnHHP were:

CHHP ($Co_4C_4H_{48}N_{24}O_{26}Cl_4$) $\rightarrow 4CO_2 + 28/3\ N_2 + 16H_2O + 16/3\ NH_3 + 2CoO + 2CoCl_2$

ZnHHP ($Zn_4C_4H_{40}N_{20}O_{26}Cl_4$) $\rightarrow 4CO_2 + 26/3\ N_2 + 16H_2O + 8/3\ NH_3 + 2ZnO + 2ZnCl_2$

All non-metal-containing products, including water, were treated as a gas. The resultant heats of detonation values **(Chart 1)** indicate that the newly prepared 2-D polymeric architectures are modestly more energetic than nickel hydrazine nitrate (NHN), the ionic-polymer of reference from the previous study, while possessing considerably lower power output than reported for CHP and NHP. Such a decrease in heats of detonation is expected due to lower perchlorate load and significantly increased structural stabilization coming from chelating hydrazinecarboxylate anion and a network of hydrogen bonds between the parallel sheets of compounds. Hence, CHHP and ZnHHP deliver power on the order of common secondary organic explosives such as TNT, tetryl, and FOX-7 while displaying moderate sensitivities, appropriate for convenient handling and intentional initiation.

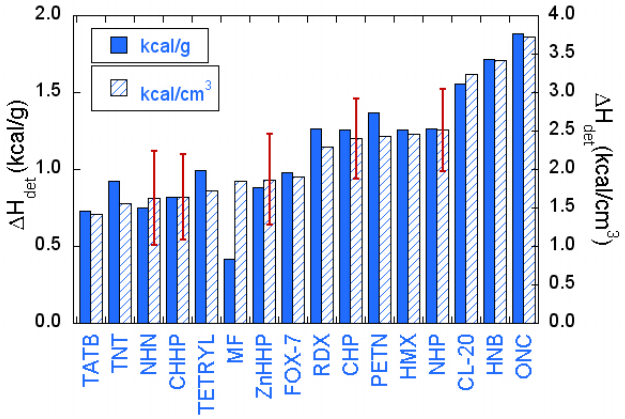

Chart 1: Bar Diagram Representation of the Literature ΔH_{det} values for eleven Highly Explosive Materials, previously reported values for CHP, NHP and NHN along with the Predicted ΔH_{det} for CHHP and ZnHHP. Error bars correspond to the 95% statistical confidence level for these values. Abbreviations used: MF (mercury fulminate), ONC (octanitrocubane). The rest are conventional energetic abbreviations.

In conclusion, two novel highly energetic two-dimensional ionic coordination polymers, CHHP and ZnHHP, were synthesized and characterized. Both structures are held together by mixed hydrazine-hydrazinecarboxylate bridges as opposed to the previously reported linear polymers, NHP and CHP, which are bridged by a single hydrazine ligand. As a result of these structural modifications, CHHP and ZnHHP possess much milder sensitivity profiles while retaining higher power content than available from typical metal-based explosives, comparable instead to those of conventional organic secondary explosives. Consequently, these species are excellent candidates for replacing heavy metal primers such as lead azide. The crystal structures represent the first example of the co-existence of the chelating hydrazinecarboxylate anion with any other anion. Careful preparative techniques allow preservation of the necessary oxidizing anion even in the presence of a very competitive anionic chelating ligand. The strategy of allowing the slow reaction of hydrazine with atmospheric CO_2 provides an elegant route to new mixed-ligand systems. Examination of the CHHP and ZnHHP structural motifs demonstrates the rich structural variety that can be accessed, even in compounds utilizing the same ligands and coordination modes (e.g. where hydrazine is *trans*-bridging or monodentate and hydrazinecarboxylate is always tridentate). Notably, slight structural differences in the two compounds amount to the change of ca. 15% in suggested power output. Hence, the choice of metal in these polymeric ionic energetic materials directs and determines the solid state structure and ultimately the energetic properties of the material.

ASSOCIATED CONTENT

Supporting Information: Complete experimental details and summary of crystallographic statistics (PDF); crystallographic CIF files for CHHP and ZnHHP. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes – Hazard Warning

The materials described in this communication pose explosive hazards in addition to the toxicity of the precursors. The preparation and handling of these materials must always be attended with the proper protective measures such as face shields, blast shields, knife-handler gloves in addition to standard laboratory personal protective equipment. The authors discourage scale up procedures.

ACKNOWLEDGMENT

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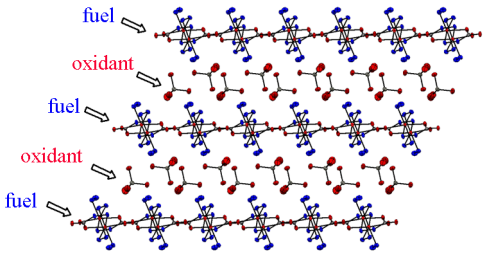
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Supplemental Information

Safer Structurally-Reinforced Ionic Polymeric Energetic Materials

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Hazard Warning and Safety Precautions

The prepared metal hydrazine hydrazinecarboxylate perchlorate complexes are very powerful energetic substances, capable of initiation by impact, friction, electric spark, heating or open flame. Utmost care and use of safety protocols (such as use of face shields, Kevlar gloves and materials least capable of static discharge) should be used at all times. Starting materials also pose danger, as hydrazine hydrate is a known carcinogen and perchloric acid and its salts are powerful oxidants.

Materials

Perchloric acid 60-62%, cobalt perchlorate hexahydrate and zinc perchlorate hexahydrate were obtained from Alfa Aesar, hydrazine hydrate 64% from Acros Organics. All reagents were used without further purification.

Syntheses

$Co_2C_2N_{10}H_{20}Cl_2O_{13}$ (**1**): Cobalt (II) perchlorate hexahydrate (40 mg, 0.11 mmol) was dissolved in 50 µL of distilled water. 100 µL of hydrazine hydrate (64%, 2 mmol) was added with stirring using a micropipette. Upon addition the solution turned orange-red. The reaction vial was covered with parafilm with several openings and placed behind a blast shield. Precipitation of the pink microcrystalline product began in 3-4 hours and proceeded to finish in 24 hours. Product was filtered, washed with hydrazine hydrate and dried in a desiccator (28 mg, 87% yield). Anal. calc. for $Co_2C_2N_{10}H_{20}Cl_2O_{13}$, 587 g/mol C, 4.10; N, 24.09; H, 3.44; Found C, 4.20; N, 23.58; H, 2.39$Zn_2C_2N_{10}H_{20}Cl_2O_{13}$

Zinc (II) perchlorate hexahydrate (40.0 mg, 0.108 mmol) was dissolved in 100 µL of distilled water, 100 µL of hydrazine hydrate (64%, 2 mmol) was added by a micropipette. The solution turned cloudy as amorphous precipitate was formed. When stirred the precipitate dissolved and formation of the needle-like crystalline product began in 6-8 hours and was completed in 48 hours. Product was filtered, washed with 0.5 mL of distilled water and air dried (24.2 mg, 76% yield). Anal. calc. for $Zn_2C_2N_{10}H_{20}Cl_2O_{13}$, 593 g/mol C, 4.04; N, 23.61; H, 3.37; Found C, 4.06; N, 23.4; H, 3.3.

Drophammer and Spark Tests

Sensitivity data was obtained by use of a home-made drop-hammer.[1] The instrument consists of a metal bar to which various weights can be attached. The bar is held at a user-specified height by an electromagnet; when the electromagnet is switched off, the bar and the weight will fall upon a flat metal surface which holds the compound of interest. Thus the weight attached to the bar and the height from which it falls can be controlled to determine the impact sensitivity of a given compound. The values for CHHP and ZnHHP are given below alongside those for CHP, which was reported earlier.[2]

Electric spark test was performed using a High Frequency Generator, Model BD-10AS Electro-Technic Products, at 115 V and 0.35 A.

Compound	Drophammer Response	ESD* Sensitivity	Flame Sensitivity	Decomposition Temperature†
CHHP	30 cm, 2.5 kg	detonates	detonates	231°C
ZnHHP	50 cm, 5 kg	insensitive	deflagrates	293°C
CHP	20 cm, 2.5 kg	detonates	detonates	194°C

* Electrostatic Discharge
† Observed via differential scanning calorimetry

1. Bushuyev, O. S.; Brown, P.; Maiti, A.; Gee, R. H.; Peterson, G. R.; Weeks, B. L.; Hope-Weeks, L. J. *J. Am. Chem. Soc.* **2012**, *134*, 1422
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Data Collection and Analyses

Elemental analysis was performed on PerkinElmer 2400 Series II CHNS/O Analyzer. X-ray diffraction data was obtained on Bruker Smart Apex II single-crystal X-ray diffractometer at 150 K or room temperature. Multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods algorithm and refined using SHELX-97 software. All hydrogen atoms were calculated from the electron density map and refined using distance restraints. A data summary for CHHP and ZnHHP is included below in Table S1. The .cif files are also available as electronic supplementary information via the Internet at http://pubs.acs.org.

Table S1 Data collection and refinement statistics summary

	Cobalt Hydrazine Hydrazinecarboxylato Perchlorate (CHHP)	Zinc Hydrazine Hydrazinecarboxylato Perchlorate (ZnHHP)
CCDC number		
Formula	$Co_2(N_2H_4)_4(N_2H_3CO_2)_2(ClO_4)_2H_2O$	$Zn_2(N_2H_4)_3(N_2H_3CO_2)_2(ClO_4)_2$
Density (g/cm^3)	2.000	2.117
Data Collection		
Crystal System	monoclinic	triclinic
Space Group	P2(1)/c	P-1
Color and Shape	orange plates	colorless needles
Cell Dimensions		
a, b, c (Å)	9.7762(9), 11.3848(11), 10.0190(9)	7.8541(6), 9.3723(7), 13.2825(10)
α, β, γ (°)	90, 114.0540(10), 90	90.2280(10), 92.1740(10), 107.4020(10)
Volume (Å^3)	1018.28(16)	931.73(12)
Z	4	2
Resolution (°)	26.37	26.73
R_{merge}	.0265	0.0176
Completeness (%)	100	99.4
Redundancy (collected reflections /independent reflections)	5.06 (10805/2085)	2.68 (10534 /3925)
Refinement		
Data/restraints/parameters	2085 / 230 / 14	3925 / 325 / 21
Goodness of fit on F^2	1.050	1.060
Final R indices [I>2σ (I)]	R1 = 0.0221,	R1 = 0.0321,
R indices (all data)	R1 = 0.0247, wR2 = 0.0604	R1 = 0.0361, wR2 = 0.0861
Largest diff. peak and hole (e. Å^{-3})	0.65, -0.31	1.14, -0.74

Complete supplemental information for these crystal structures is available in the Crystallographic Information files (.cif files) from the Cambridge Crystallographic Data Centre using the accession codes listed above.

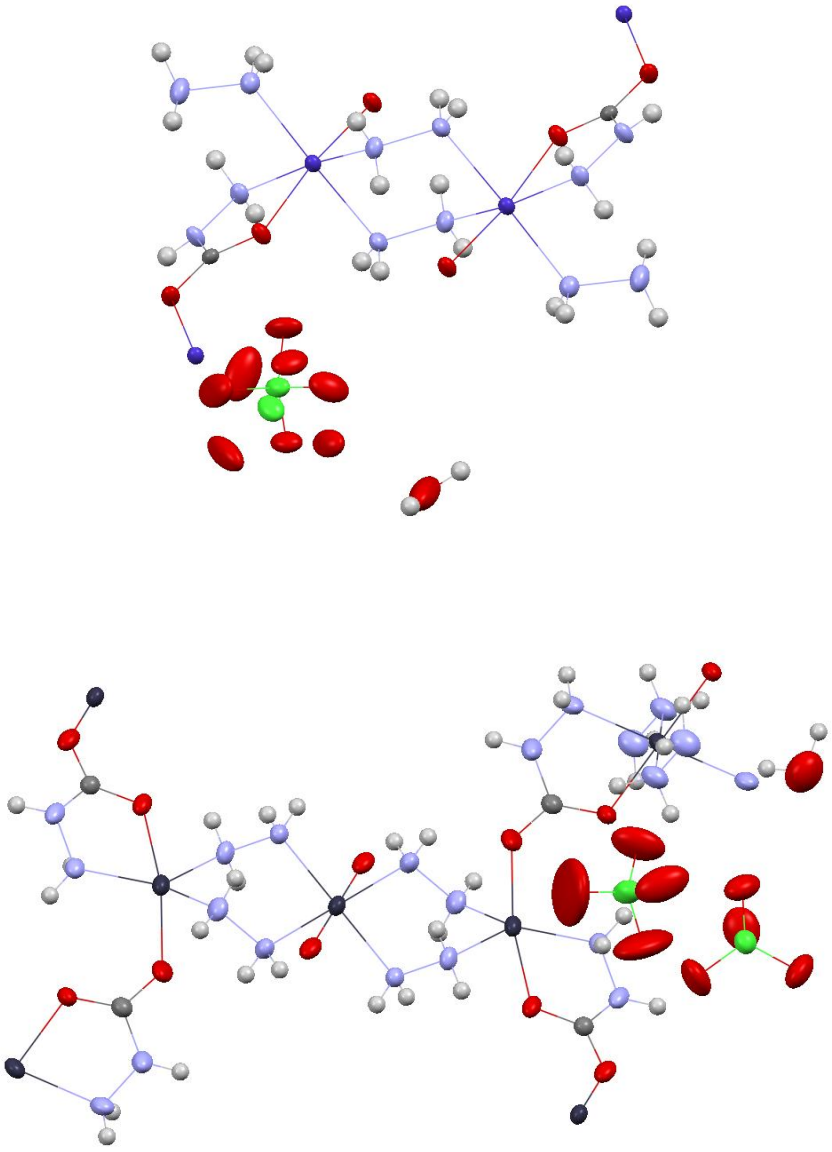

Figure S2 Structure drawing of CHHP (top) and ZnHHP (bottom). Ellipsoids drawn at 50% probability.